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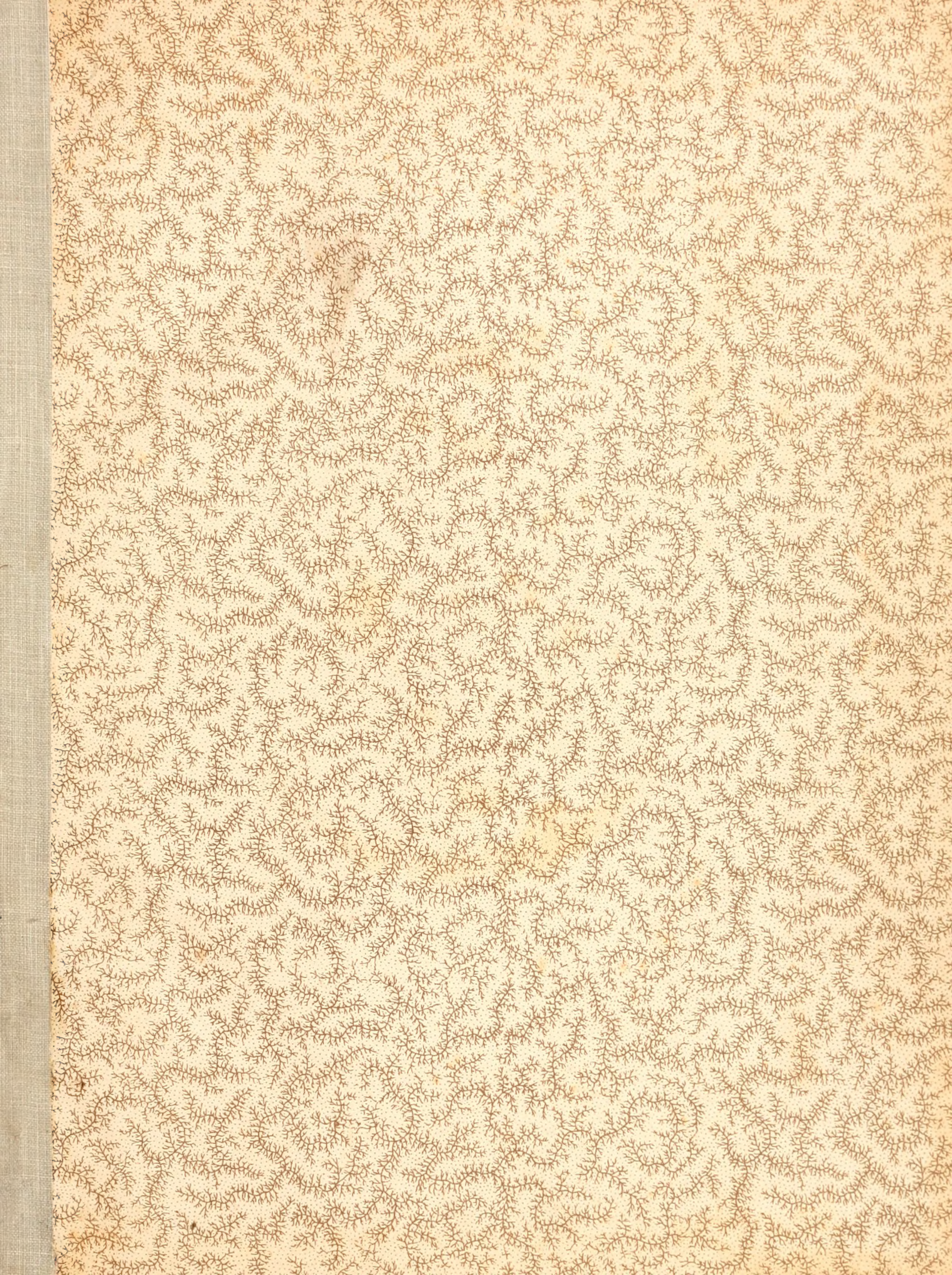

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May 29/91

Sulphon-phthaleins
obtained from
Ortho-sulpho-paratoluic Acid

Dissertation

Presented to the Board of University Studies of the Johns-Hopkins University for the degree of Doctor of Philosophy

by

Walter Jones.

1891.

54394

Preparation of Para-methyl-sulphon-fluorescein [illegible] [illegible]
[illegible] 29
[illegible] 30
Treatment of Para-methyl-sulphon-fluorescein
with Acetic Anhydride 31.
[illegible]
with Phosphorus Pentachloride 32.
Reduction of Para-methyl-sulphon-fluorescein 33.
Treatment of Para-methyl-sulphon-fluorescein with
[illegible]
Treatment of Para-methyl-sulphon-fluorescein with
Phosphorus Pentachloride 34.
Treatment of Para-methyl-sulphon-fluorescein
with Bromine
[illegible]
[illegible]
[illegible]
Biographical 42

[illegible]

chemical reaction than the [illegible] upon the

phthalimide. The first compound of this class was prepared

by the action of nitric acid on phthalic anhydride, but

owing to experimental difficulties its investigation was

[illegible]

was subsequently [illegible] by [illegible] compound

compound [illegible] from the [illegible]

[illegible] in the presence of [illegible] and [illegible]

[illegible] at first only [illegible]

The equation

[illegible] compound which [illegible]

[illegible] d. d. chem. Ges. IV. 757; 556. 907. [illegible] Chem. [illegible]

has been obtained by [illegible] [illegible] [illegible] [illegible] [illegible] the [illegible] of [illegible] [illegible] [illegible] [illegible] should be [illegible] the [illegible] formula:

$$C_6H_4 < \begin{array}{l} CO.C_6H_4(OH) \\ CO.C_6H_4(OH) \end{array}$$

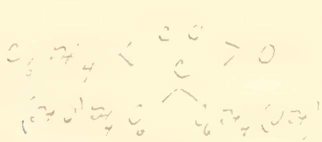
By a subsequent study of them by [illegible] [illegible] [illegible]

[illegible]

[illegible] [illegible] [illegible] in the presence of a [illegible] [illegible] — [illegible] fact which it would be difficult [illegible] [illegible] [illegible] explanation by the following considerations.

[illegible] [illegible] [illegible] compound [illegible] [illegible] [illegible] [illegible] by [illegible] reactions, [illegible] would [illegible] [illegible] [illegible] [illegible] by one or the other of these two formulae:

I



$$C_6H_4 < \begin{array}{c} CO \\ C \end{array} > O \qquad (HO)H_4C_6 \; C_6H_4(OH)$$

II

$$C_6H_4 < \begin{array}{l} CO.C_6H_4\,OH \\ CO.C_6H_4 \end{array}$$

[illegible]

[illegible]

[illegible]

The constitution of [illegible] formula [illegible]

[illegible] C_6H_4 [illegible] which [illegible]

made from phthalic [illegible] by [illegible]

[illegible] that phthalyl chloride should [illegible]

by an unsymmetrical formula C_6H_4 [illegible].

When the latter is treated with benzene in the presence of

aluminum chloride, a compound is obtained which

Friedel and Crafts assigned the formula [illegible]

but which Von Baeyer found capable of taking up water

in the presence of a reducing agent, forming an acid

of the composition [illegible], which in turn loses [illegible]

[illegible]

[illegible]. This [illegible]

[illegible] that the [illegible] formed in the [illegible]

[illegible] Friedel and [illegible]

[illegible]

phenol-phthalein; for, on heating [illegible] [illegible] [illegible] nitric acid, [illegible] the [illegible] the former, and [illegible] the remaining [illegible] [illegible] [illegible] phenol phthalein is obtained.

[illegible]

which can be more [illegible]

[illegible]

[illegible]

It was also found in the course of the work that there can be obtained by heating the cylinder [illegible] the distance between [illegible]

[illegible]

$$[illegible]$$

[illegible]

[illegible] from the [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

by heating [illegible] -sulphonic acid [illegible] was studied by [illegible] and [illegible]* which they found to take place according to the equation

[illegible]

[illegible] I. By heating [illegible] which [illegible] II. By heating the anhydrous [illegible]

[illegible]

[illegible]

[illegible]

[illegible] preceded by the [illegible] station which had been undertaken by [illegible]. 200 grams of the sublimate and 300 grams of [illegible] building [illegible] of the [illegible] and the [illegible] of the [illegible] beginning of [illegible] of the [illegible]. When the sublimate [illegible]

[illegible]

[illegible]

[illegible] minutes [illegible] bubbling [illegible] until the

the droplets of water vapor formed in the [illegible] and

[illegible] can be seen on the [illegible] of the tube [illegible]

[illegible] becomes [illegible] of gaseous [illegible]

[illegible] no [illegible] further [illegible]

[illegible] during the heating [illegible]

of the [illegible] material for [illegible] the

almost [illegible] The [illegible]

necessary condition for the completion of the [illegible]

After cooling, the [illegible]

[illegible] is extracted with water and the [illegible]

[illegible]

[illegible]

[illegible]

[illegible] grams of the salt [illegible] grams of [illegible]

[illegible] grams of [illegible]

[illegible] grams of the salt [illegible] grams of [illegible]

[illegible] grams of the salt gave [illegible] grams of [illegible]

[illegible] Found

The result of these analyses shows that the [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

---

[1] [illegible] page [illegible]

[2] Am. Chem. [illegible] 5-205

[3] Am. Chem. [illegible] 2-220

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] from [illegible]

[illegible] from [illegible]

[illegible] when they [illegible]. The [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

The acid [illegible] [illegible]

completely [illegible] [illegible]

considerable [illegible]

[illegible]

hydrogen and the acid sulphate present (?). The solution was then evaporated almost to dryness before any precipi-[illegible] at once, and the material had a decidedly reddish [illegible] color due probably to decomposition caused by the con-

[illegible]

and subsequently [illegible] of the free [illegible] in water. After this it [illegible]

[illegible]

[illegible] appropriate [illegible] and the heating was continued. After the material had stood for a few days

[illegible]

[illegible]

[illegible]

[illegible] crystallized [illegible]

[illegible] of this acid [illegible] determination of the acid of crystallization. The analysis [illegible] for carbon, hydrogen and sulphur [illegible]

molecules $C_6H_3(SO_3H) [illegible] + H_2O$

.2287 gram of the crystallized acid gave [illegible] gram of [illegible]

.2270 gram of the crystallized acid gave [illegible] gram of [illegible]

.4700 gram of the crystallized acid gave .0870 gram of H_2O and .2297 gram of CO_2

.5109 gram of the crystallized acid gave .0850 gram of H_2O and .2058 gram of CO_2

[illegible]	8.24	8.41	8.505		
[illegible]	44.20			44.01	44.02
[illegible]	5.25			5.11	5.44

It may be stated in general that the salts of this acid were

[illegible] on all the compounds which were [illegible] ex-
[illegible]. The silver salt [illegible] with [illegible] the same salt
[illegible], while the ammonium salt can be obtained
in good crystalline condition if the crystallization be carried
on [illegible] with sufficient care. The [illegible] of the
salt of calcium [illegible] and lead [illegible] [illegible]
them by crystallization. The [illegible] salt [illegible]
[illegible]

[illegible] solvent which were used. All of the metallic salts of
[illegible] were made by treating a solution of

[illegible] with [illegible] and by [illegible]
[illegible] with [illegible]

The course of crystallization in some of these [illegible]
[illegible]

[illegible] They were [illegible]

[illegible]

[illegible] of the [illegible]

[illegible]

[illegible]

[illegible] several places with the [illegible]

[illegible]

[illegible]

[illegible] with the [illegible]

[illegible] of the [illegible]

[illegible]

[illegible] of the [illegible]

[illegible]

[illegible] to the [illegible]

the nitrogen of the soil [illegible] the [illegible]

[illegible] brought [illegible]

[illegible] of [illegible] the [illegible]

analysis. The [illegible] was determined by the method of

igniting the soil and then extracting with [illegible] acid.

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] detected. [illegible]

solution still warm was treated with barium carbonate

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] analysis of the [illegible] obtained in the first experi-
ment gave the following results.

.2262 grams of the salt gave .1262 grams of [illegible]

and .0025 grams of [illegible]

[illegible] grams of the salt gave [illegible] grams of [illegible]

[illegible]

[illegible] The [illegible] [illegible] [illegible]
[illegible] of the [illegible]
[illegible] the light [illegible]
[illegible]

[illegible]
The border of the [illegible]
[illegible]
[illegible]

[illegible] of [illegible] the [illegible]
[illegible]

[illegible]

[illegible]

[illegible] year 1884 [illegible]

[illegible] 55 [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] upon the following [illegible]

[illegible]

[illegible] grams of [illegible] grams of [illegible]

[illegible] sulphuric acid bath at 100° [illegible] the reaction [illegible] small bulbs of phosphorus pentachloride were added from time to time. When the evolution of gas had ceased the flask containing the product of the reaction was cooled and the material washed with water. This method [illegible] [illegible] was found [illegible] microscopic [illegible]

[illegible] in [illegible] dark blue [illegible] and the solution does not show fluorescence. – The analyses of the compound correspond with the combination of hydrazo ben-zene [illegible] fluorescine in which [illegible] hydrogen atoms have been replaced by chlorine, a compound which in all probability should be represented by the formula.

$$[illegible]$$

The analysis of the compound gave the following results:–

[illegible]

$C_{25}H_{15}SO_3Cu, 4H_2O$

According to the directions given by Fresenius [illegible] of

[illegible]

weight of [illegible]

bromine [illegible] through bromine the

[illegible]

bromine. The mass was filtered, washed with [illegible]

[illegible]

found to contain only a trace of bromine, perhaps mechanically held, the experiment was repeated in a flask so that the water could be shaken together. Then the new arrangement of bromine was added (3 equivalents), and the mixture left

[illegible]

to stand over night. It was washed with [illegible] which was driven off by continued heating [illegible] the [illegible] having been [illegible]

[illegible]

[illegible]

The residue [illegible] was found [illegible] with [illegible]

[illegible]

[illegible]

[illegible]

[illegible] of the [illegible]

[illegible]

[illegible]

[illegible]

[illegible] suppose that when [illegible] of the phenol [illegible] saturated with [illegible] of the phenol [illegible] equivalents of the [illegible] would be formed [illegible]

[illegible]

containing two acid residues — that is the sulphonphthalein just described. Experiment shows however that when the proportions of the two substances act on each other, a sulpho-

[illegible]

and moreover when such proportions of the acid and the phenol are employed as should be theoretically required for the formation of the sulphonphthalein with four residues there is then formed a sulphonphthalein containing six acid residues. This last result is also reached when any excess of the phenol is used [illegible]

[illegible]

[illegible] was based on the result of the experiments which are described below. While [illegible]

[illegible]

[illegible]

[illegible]

and at slightly elevated temperatures, to cause the union

[illegible]

markable fluorescent [illegible] solutions which characterize

compounds belonging to the class of phthaleins, together with

[illegible]

[illegible] as the complex

sulphon-phthaleins mentioned before (page 5.)

Experiment I. 2½ parts of ortho-sulpho-benzoic acid

and one part of resorcin (one equivalent of the acid and one

[illegible]

At times the contents of the tube were [illegible]

materials which was [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] I II III

The method of procedure [illegible]

[illegible]

[illegible]

[illegible]

[illegible] grams of the hydrocarbon [illegible] gave [illegible] grams of

H_2O.

[illegible] grams of the hydrocarbon [illegible] gave [illegible] grams of CO_2

and [illegible] grams of H_2O.

[illegible] grams of the [illegible] gave [illegible] grams of CO_2

and [illegible] grams of H_2O.

[illegible] grams of the hydrocarbon [illegible] gave [illegible] grams of [illegible]

[illegible] grams of the hydrocarbon [illegible] gave [illegible] grams of [illegible]

Found.

[illegible]

[illegible]

[illegible]

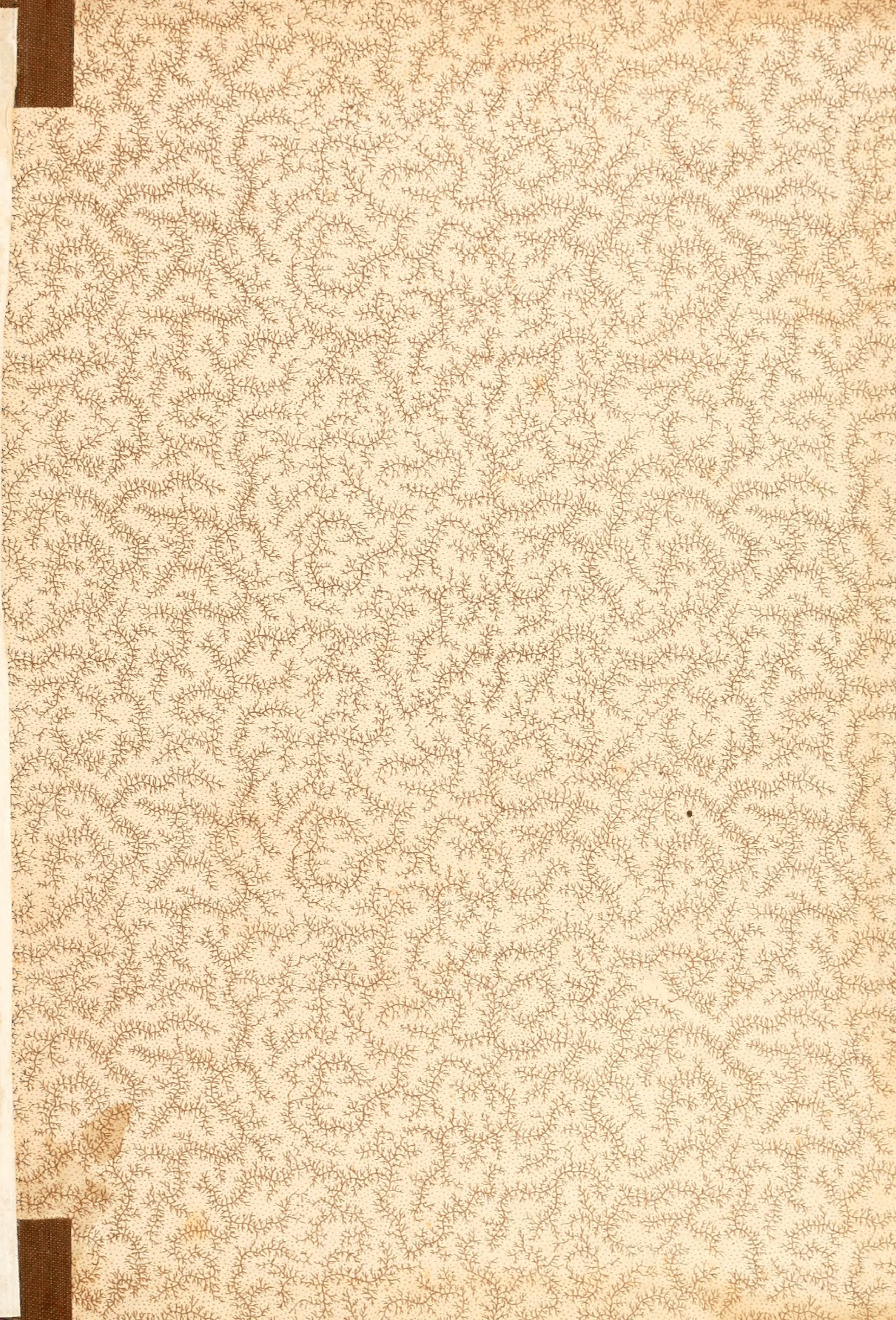
[illegible]

[illegible] and subsequently for [illegible]

[illegible]

[illegible] can be suppressed by [illegible] but not by [illegible]

[illegible]

[illegible]